Electronic Supplementary Material (ESI) for Materials Advances.

Dispersing uncharged cellulose nanocrystals through a precipitation surface modification route using oligosaccharides

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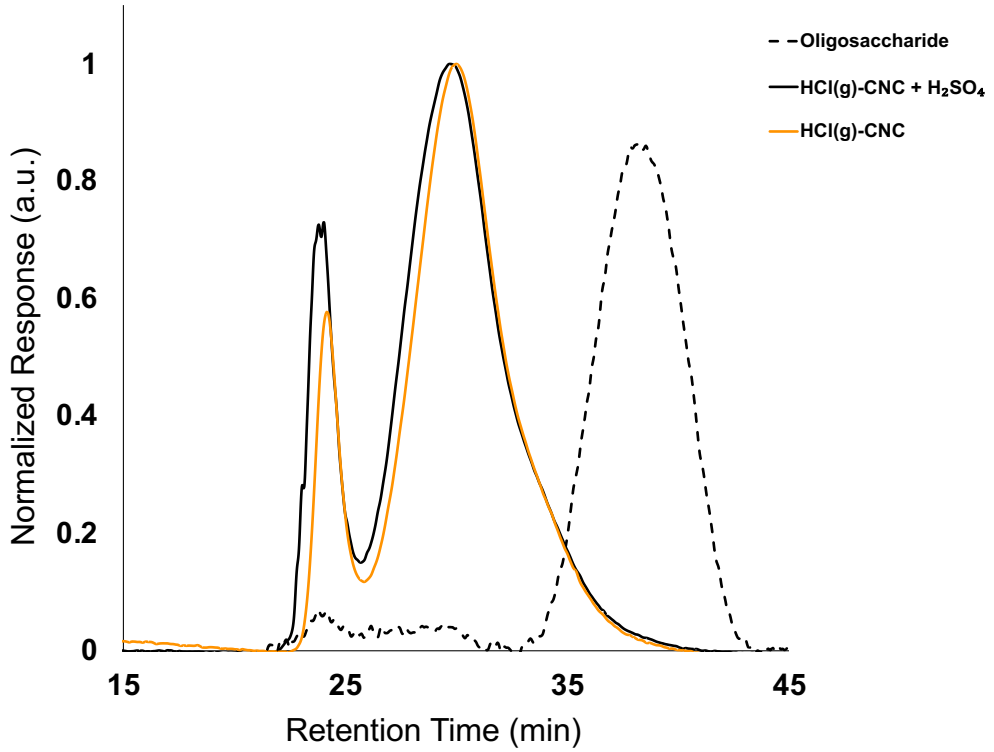

Figure S1. Molecular weight distributions of HCl(g)-hydrolysed CNCs before and after exposure to ca. 9 wt.% H_2SO_4(aq) Also shown, is the molecular weight distribution of the oligosaccharide surface modifiers.

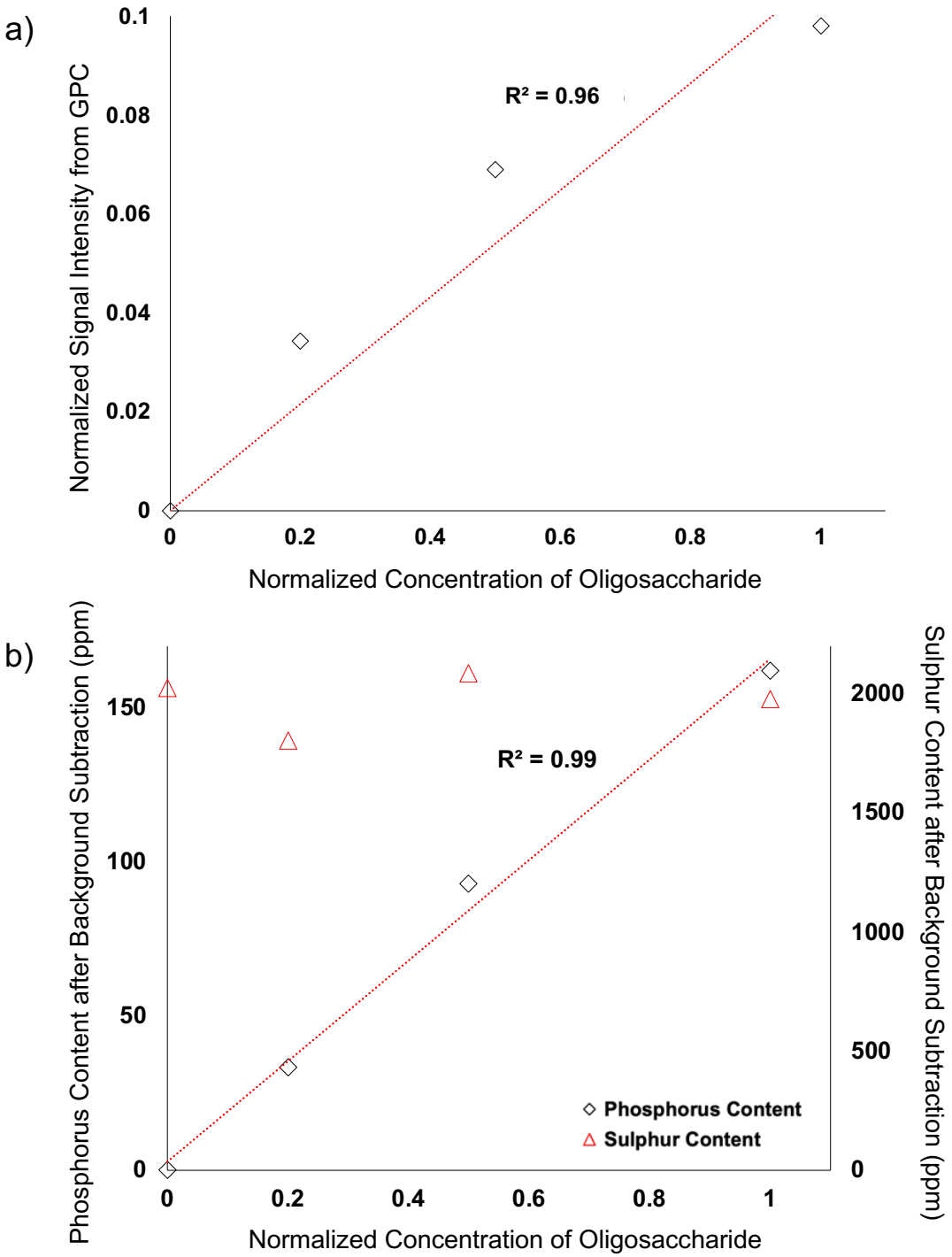

Figure S2. Linear plots of a) the increasing intensity of the oligosaccharide peaks as measured by GPC and b) the increasing normalized phosphorous concentration as a function of normalized oligosaccharide concentration on HCl(g)-CNCs. Also shown is the constant sulphur content of the HCl(g)-CNCs after exposure to sulphuric acid, and after oligosaccharide surface modification.

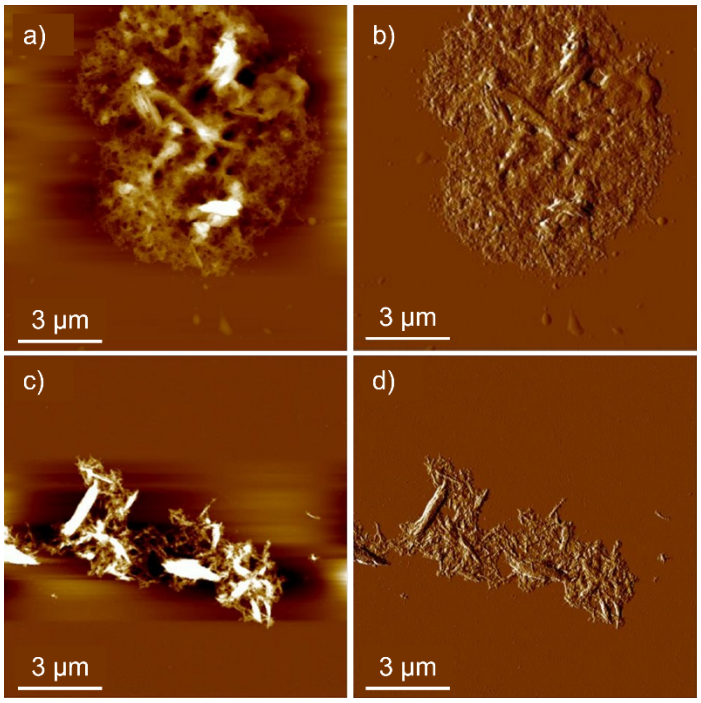

Figure S3. Atomic force microscopy height images of a) HCl gas hydrolysed Whatman 1 filter paper prior to ultrasonication and c) after 15 min of ultrasonication. Also shown are the corresponding amplitude images for b) HCl gas hydrolyses Whatman 1 filter paper prior to ultrasonication and d) after 15 min of ultrasonication.

Table S1. Sulphur and phosphorus content as measured by ICP-OES elemental analysis of HCl(aq)-CNCs before and after exposure to sulphuric acid, and after oligosaccharide surface modification.

	Sulphur content (ppm)	**Phosphorous content (ppm)**
H(aq)-CNC	53 ± 1	14 ± 3
H(aq)-CNC + H_2SO_4 (control)	2350 ± 10	9 ± 3
H(aq)-CNC + Oligo (1:1)	2630 ± 30	186 ± 5
H(aq)-CNC + Oligo (1:0.5)	2690 ± 10	100 ± 4
H(aq)-CNC + Oligo (1:0.2)	2720 ± 40	64 ± 7

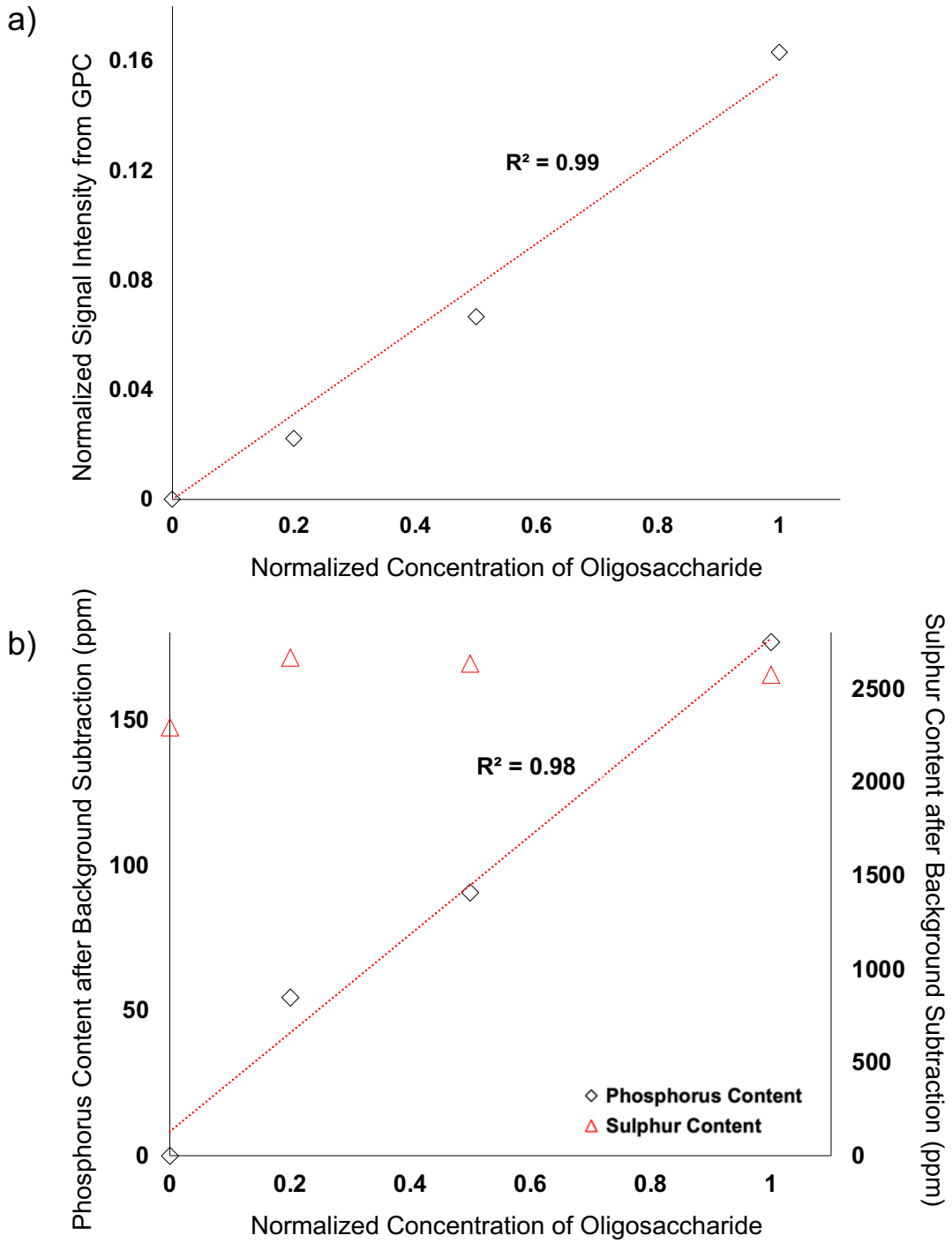

Figure S4. Linear plots of a) the increasing intensity of the oligosaccharide peaks as measured by GPC and b) the increasing normalized phosphorous concentration as a function of normalized oligosaccharide concentration on H(aq)-CNCs. Also shown is the constant sulphur content of the HCl(aq)-CNCs (red triangles) after exposure to sulphuric acid, and after oligosaccharide surface modification.

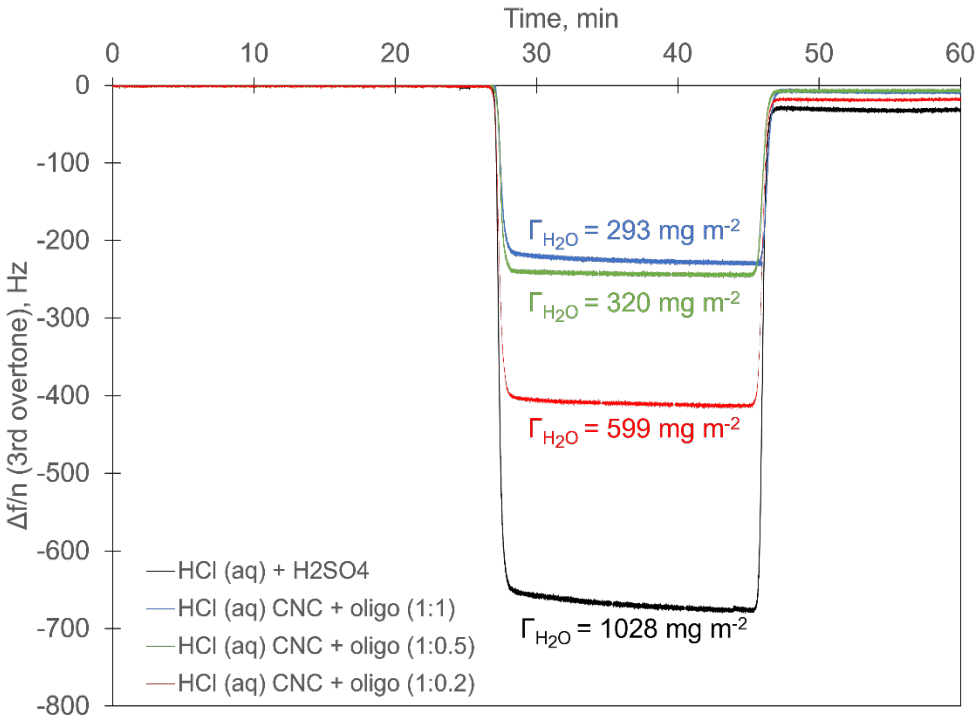

Figure S5. Change in normalized resonance frequency (3rd harmonic) as a result of a water/deuterium oxide solvent exchange as measured by quartz crystal microgravimetry, for the control sample HCl(aq)-CNCs + H_2SO_4 and oligosaccharide modified samples.

Yield of oligosaccharide precipitation calculation

Table S2. Yield of oligosaccharide precipitation on HCl(g) CNCs during *post hydrolysis* surface modification based on theoretical maximum of phosphorous content at 100% precipitation.

	Mass of CNCs g	Mass of oligosacch-arides g	Theoretical P content in mass of CNCs ppm	Theoretical P content in mass of oligosaccharides ppm	Theoretic P content ppm	Measured P content ppm	Yield of precipitation %
HCl(g) CNC + Oligo (1:1)	0.09	0.09	2.97	51.66	304	170	56.0
HCl(g) CNC + Oligo (1:0.5)	0.09	0.045	2.97	25.83	213	99	46.4
HCl(g) CNC + Oligo (1:0.2)	0.09	0.018	2.97	10.332	123	39	31.7

$$\text{Theoretical [P]}_{\text{H (g)}CNC+oligo} = [P]_{H\,(g)\,CNC+H2SO4} \times m_{CNC}$$

$$\text{Theoretical [P]}_{Oligosaccharide} = [P]_{Oligosaccharide\ control} \times m_{oligosaccharide}$$

$$\text{Theoretical [P]}_{\text{100\% oligosaccharide precipitation}} = \frac{Theoretical\ \text{[P]}_{\text{H (g)}CNC+oligo} + \ Theoretical \text{[P]}_{Oligosaccharide}}{m_{CNC} + m_{oligosaccharide}}$$

$$Yield\ of\ precipitation = \frac{[P]_{Meausred}}{\text{Theoretical [P]}_{\text{100\% oligosaccharide precipitation}}} \times 100$$

Supporting Results and Discussion

High molecular weight peak presence in GPC analyses. There are other significant peaks at ca. 24 min in the Figures 3 and 6 GPC traces that represent higher molecular weight polymer presences. While possible this may be the result of an unhydrolyzed cellulose presence in the sample, we ultimately consider this to be unlikely since such high molecular weight peaks have not been observed for samples hydrolyzed with HCl(g) when dissolved in dimethylacetamide/LiCl solution for GPC analyses in the past.[1] Thus, we consider it is more likely that the high molecular weight peaks at ca. 24 min in the Figures 3 and 6 GPC traces are an artifact of the carbanilation reaction used to make these cellulose polymers soluble in DMSO for GPC analyses. We hypothesize that complete carbanilation of our cellulose materials to a DS of 3 did not occur. As such, there were cellulose fractions made only partially soluble in DMSO which resulted in a higher molecular weight peak being present at ca. 24 min in the GPC analyses. Also of note is that the peak at ca. 24 min in the Figure 6 GPC trace is much lower in intensity than the analogous peak in the Figure 3 GPC trace relative to the CNC peaks. This supports our hypothesis that this peak is the result of an artifact caused by incomplete carbanilation. Since aqueous conditions for hydrolysis break down the cellulose fibre geometry, the cellulose polymers that make up CNCs thus become more accessible to

subsequent carbanilation. In contrast the HCl(g) does not change the macroscopic morphology of the cellulose polymers and as such makes the fibres less accessible to reagents.[2]

Supporting References

1 E. Kontturi, A. Meriluoto, P. A. Penttilä, N. Baccile, J.-M. Malho, A. Potthast, T. Rosenau, J. Ruokolainen, R. Serimaa, J. Laine and H. Sixta, *Angew Chem*, 2016, **128**, 14671–14674.

2 I. Solala, C. Driemeier, A. Mautner, P.A. Penttilä, J. Seitsonen, M. Leppänen, K. Mihhels, and E. Kontturi. *Macromol. Rapid Commun.* 2021, **42**, 2100092.